Nanophotonics

Hybrid light–matter states in self-assembling cavities

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Tiny flakes of metal suspended in a solution have been observed to self-assemble into pairs separated by a narrow gap – offering a tunable system for studying combinations of light and matter known as polaritons. See p.214

Stable physical systems generally require a balance between attractive forces that pull their components together and repulsive forces that push them apart. For example, Earth's gravity pulls us down, but our feet do not sink through the floor because of the overall repulsive electrical forces between the electrons and nuclei that both we and the floor are made of. On a microscopic level, the stability of materials is due to the electrostatic interaction between charged electrons and nuclei, with like charges repelling and opposite charges attracting each other. On page 214, Munkhbat *et al.*[1] report that a different balance of attraction and repulsion can cause two or more microscopic metal flakes to form an optical cavity by self-assembly – generating a pair of mirrors that can trap light between them. Such cavities have a wide range of uses because they modify the interaction between light and matter within them.

In their experiments, Munkhbat and colleagues immersed metal flakes in a solution of an organic ionic compound. Each flake becomes covered with the dissolved ions, leading to electrostatic repulsion between the flakes (Fig. 1). A counterbalancing attractive force is provided by a hidden dynamic process similar to an electron 'dance': the random motion of electrons in one flake produces electromagnetic fluctuations that influence the movement of electrons in a nearby flake. The resulting synchronized movement generates an attractive force that is known either as the Casimir force (if the wave character of the electromagnetic fields is considered) or the van der Waals force (if it is not).

Munkhbat *et al.* observed that, when two metal flakes diffusing in solution meet randomly, the balance between repulsion and attraction causes them to spontaneously assemble into a pair separated by an equilibrium distance of 100–200 nanometres. This distance is a lot smaller than the diameter of the flakes, which is several micrometres. The self-assembly also occurs for stacks of more than two flakes, and for a single flake close to a metal film attached to a silica (SiO_2) substrate. The process differs from that of other systems that similarly self-assemble as a result of the balance between electrostatic and fluctuation-induced forces – such as nanoparticles suspended in a solution, which are separated by much smaller distances in their assemblies[2].

Crucially, the inter-flake separation in Munkhbat and colleagues' system is large enough for pairs of assembled flakes to act as optical cavities for visible wavelengths of light. Optical cavities trap only certain wavelengths – those that enable the light to form a standing wave between the two mirrors (or the flakes, in the current experiments). In the same way as the length of a piano string determines the frequencies at which it can oscillate and, therefore, the note produced when struck, the length of an optical cavity determines the wavelengths of light that can be trapped.

This constraint on the possible wavelengths has a surprising consequence, known as the Purcell effect[3]: the interaction of light and matter inside a cavity is 'concentrated' at those few wavelengths. This means that the fundamental processes that lead to light emission and absorption are enhanced or suppressed within the cavity (compared with what happens in free space), depending on whether these processes take place at wavelengths that are allowed or forbidden, respectively. The interaction of light and matter in a material can therefore be substantially modified simply by putting the material inside a cavity[4].

A particularly striking effect occurs when the interaction is enhanced so much that photons emitted by matter inside a cavity are reabsorbed by the same matter before they have a chance to leave through the mirrors. In this scenario, known as the strong-coupling regime, the cavity no longer contains photons. Instead, it contains polaritons[5] – hybrids of light and excited matter that can be thought of as photons that are continuously absorbed and re-emitted by the matter inside the cavity. Munkhbat *et al.* demonstrate that their self-assembled cavities can reach the strong-coupling regime and support polariton formation.

Polaritons inherit properties of both of their constituents, such as the extremely small mass of the photons and the ability of the excitations in matter to interact. The resulting combination of properties enables behaviour that is not shown by either of the constituent systems alone. For example, polaritons can collapse

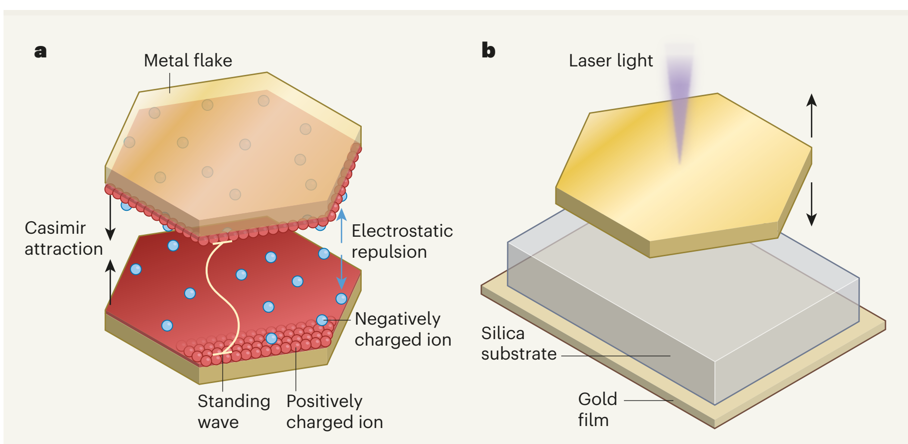

Figure 1 | How optical cavities self-assemble from metal flakes. a, Munkhbat *et al.*[1] suspended micrometre-scale metal flakes in a solution of an organic ionic compound containing positively and negatively charged ions. The ions associate with the flakes' surfaces, to produce a double layer of ions with a net positive charge, causing flakes to repel each other. A counterbalancing attractive force (known as the Casimir force) arises through random electron motion in the flakes. As a result, neighbouring flakes self-assemble into pairs, and their separation is determined by the balance of repulsion and attraction. The flakes act as optical cavities – pairs of mirrors that trap light at certain frequencies to form a standing wave of light. The flake separation can be tuned by altering the concentration of the solution. **b**, Optical cavities also assemble from flakes and gold films attached to silica substrates. A laser beam shone on the flake can exert an extra force that alters the separation in a time-dependent way.

into the same quantum state (a process called Bose–Einstein condensation), thereby producing a macroscopic quantum state that emits coherent light, like a laser[6].

Another fascinating consequence of the strong-coupling regime is that the properties of the material in the cavity can also change. For instance, the rates of photochemical reactions, which occur when a molecule has been excited by absorbing a photon, can be modified in a cavity when the excited state is a polariton[7]. Moreover, the photons in a cavity interact simultaneously with all the molecules present — the polaritons can therefore be thought of as the collective excited states of a 'supermolecule' that is formed from all the individual molecules. This potentially opens up reaction pathways that are not available to isolated molecules outside the cavity[8], and can enable energy to be transferred between molecules over much larger distances than would otherwise be possible[9,10].

Given the interest in polaritons, a highlight of Munkhbat and colleagues' findings is that the distance between the mirrors in their self-assembled cavities can be adjusted in two ways, potentially allowing cavities to generate polaritons from different materials, and providing a way to control the composition (the proportions of light and matter) and energies of polaritons. The first approach is to change the concentration of the dissolved ionic compound so as to alter the charge of the ion layer that forms around the metal flakes.

The second approach is more dynamic, and was used in a cavity system that assembled from a flake and a metal film attached to a silica substrate: by shining a laser on the flake, an extra force was exerted on it, thus allowing time-dependent control of the flake separation in a single self-assembled cavity. This could enable strong coupling to be turned on and off at will — which would enable fascinating applications, such as systems in which polariton-enabled chemical reactions are controllably activated or deactivated, or in which energy-transfer pathways between molecules can be modified to alter the colour or intensity of emitted light.

However, the sensitivity of the flakes to external lasers is a drawback for some studies. For example, an optical technique called nonlinear spectroscopy can be used to reveal detailed information about polariton systems[11], and polaritons are condensed[6] to enable the investigation of macroscopic quantum states. Both types of study require the use of relatively strong laser fields that would disrupt the delicate balance of forces holding the self-assembled cavities in place, thereby destroying the cavities. Nevertheless, Munkhbat and colleagues' discovery of tunable, self-assembling optical cavities provides a versatile experimental platform for investigating polaritons, and adds to the repertoire of self-assembly techniques that can be used by scientists more generally.

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The author declares no competing interests.